

Convention Dates
(Switzerland)Corresponding Applications
in United KingdomJan. 22, 1941;
Nov. 27, 1941;No. 809/42 } dated Jan. 20, 1942.
No. 810/42 }

(One Complete Specification Left under Section 91 (2) of the Patents and Designs Acts, 1907 to 1942).

Specification Accepted: Aug. 23, 1943.

COMPLETE SPECIFICATION

Manufacture of Alcohol-Soluble Dyestuffs

We, J. R. GEIGY, A.-G., a body corporate organised according to the laws of Switzerland, of 215, Schwarzwaldallee, Basle, Switzerland, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the manufacture of alcohol-soluble dyestuffs, and aims to produce such dyestuffs having useful properties.

According to the invention new valuable alcohol-soluble dyestuff salts are produced by precipitating azo dyestuffs, which contain acid groups making them water-soluble, and also at least one hydroxyl group acylated by an aryl sulphonic acid, with or by means of basic dyestuffs.

The new water-insoluble compounds are distinguished from similar known dyestuff salts of acid and basic dyestuffs, by an improved alcohol-solubility, throughout by greater light fastness and generally by purer colour shades. Furthermore, in comparison with improved dyestuff salts, which contain complex metal compounds and are therefore not directly comparable, the compounds produced according to this invention prove superior in alcohol solubility, in the pure colour shades and in many cases also in light fastness.

The acid dyestuffs used as starting-material are prepared by the well-known method of building up azo dyestuffs. The final esterification of the phenolic group is performed in a weakly acid solution with *p*-toluene sulphonyl chloride in the presence of sodium acetate. The formulæ given in each case are self-explanatory.

Furthermore, it has been found that when using azo dyestuffs, which contain a plurality of sulphonic acid groups, and which therefore require more than molecular quantities of basic dyestuff for precipitation, a portion of the basic dyestuffs can be replaced by other organic bases

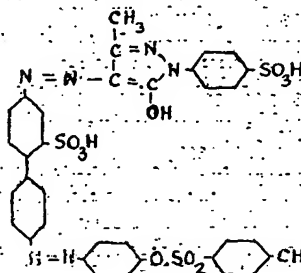
which are also suitable for precipitating acid dyestuffs.

As organic bases there particularly come in question those of the aromatic series, such as aniline, toluidines, xylidines, aminodiphenyl compounds, their substitution products, aryl guanidines and arylbiguanides. A more detailed enumeration is unnecessary as these compounds have become known for similar purposes in large numbers and are mentioned in publications, especially in patent literature.

In consequence of the reduction in the amount of the basic dyestuff components the colour shade of these alcohol soluble dyestuffs approaches more closely that of the acid components. The properties, especially the fastness properties are as good as those of the compounds which consist only of basic and acid dyestuffs.

In the following Examples the parts are by weight, and the temperatures are Centigrade.

EXAMPLE 1.



50 Parts of this dyestuff are dissolved hot in 2500 parts of water, the solution is filtered if necessary and precipitation is effected by a solution of 72 parts of rhodamine 6 G extra (Schultz, dyestuff tables, 7th Edition, No. 866) in 1800 parts of water and 36 parts of 80% acetic acid at 60–70°. When the precipitation is complete, stirring is continued for a quarter of an hour and then filtration is

[Price 1/-]

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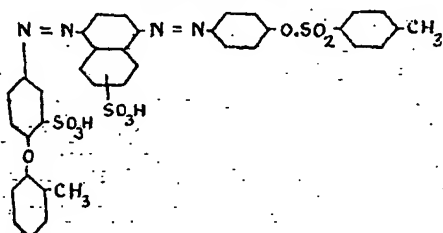
effected.

The new yellow-brown crystalline compound dissolves, even in the cold, to the extent of 10% and more in alcohol, it colours cellulose ester lacquers with pure orange colour of very good light fastness.

When the acid dyestuff is precipitated by rhodamine B (Schultz No. 864) a crystallised brown powder is obtained of which the solubility in alcohol is excellent even in the cold.

The colorations in cellulose ester lacquers are characterised with a good light fastness by an extraordinary purity and brilliance.

EXAMPLE 2.

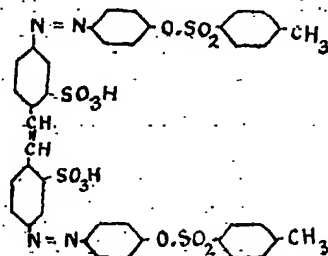


50 Parts of this dyestuff are dissolved hot in 2500 parts of water and precipitated at 55—60° by a solution of 87.5 parts of rhodamine 6 G extra in 2000 parts of water and 45 parts of 80% acetic acid. The whole is heated to 75°, whereby the new compound is precipitated in crystallised form of brown appearance. It produces coatings of pure orange colour and is soluble in the cold to more than 10% in alcohol. The colorations are waterfast and of excellent light fastness, which is very surprising, when it is remembered that 65—70% of the new compound consists actually of not fast basic dyestuff.

When precipitation is effected by rhodamine B (Schultz No. 864) a crystallised brown compound is obtained of excellent solubility, of which the beautiful, pure red colorations exhibit an unexceptionable water fastness with a very good light fastness.

Even auramine OO (Schultz No. 752) produces a precipitate which is soluble in cellulose ester lacquers with a beautiful yellow colour. The light fastness is excellent.

EXAMPLE 3.



100 Parts of this technical dyestuff are dissolved hot in 2000 parts of water and precipitated at 60—70° by a solution of 90 parts of rhodamine B extra in 1500 parts of water and 30 parts of 80% acetic acid. The crystalline compound possesses an excellent alcohol solubility and produces, for example in nitro-cellulose lacquers pure red colorations of excellent light fastness.

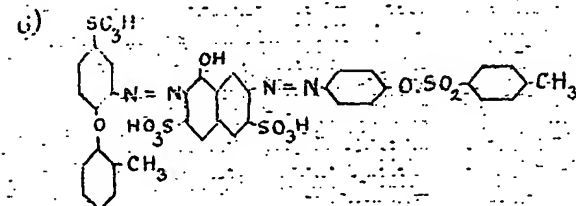
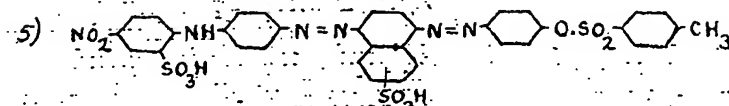
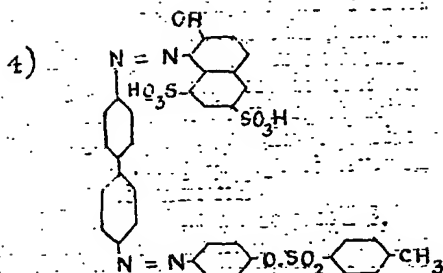
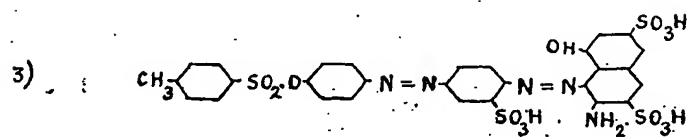
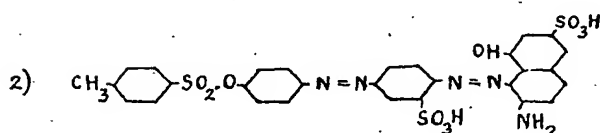
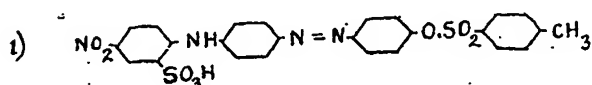
In comparison with a similar compound obtainable from chrysophenine (Schultz No. 726) and rhodamine B, the precipitate produced according to the above example proves considerably more lightfast, purer in colour shade and much more soluble in alcohol. The chrysophenine lacquer is difficultly soluble in alcohol; also in other usual solvents and cellulose ester lacquers. It leaves such large residues that it is not practical to use. From this comparison it will thus be seen that the phenolic hydroxyl group, esterified by an aryl sulphonic acid, is the cause of the surprising improvements in the properties of the compounds produced according to the invention. This is the more surprising as actually alkoxy groups are known as very suitable substituents for dyestuffs with excellent solubility in organic solvents.

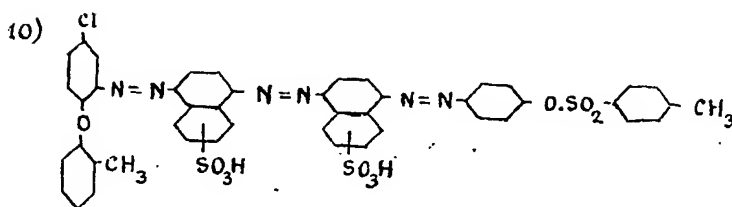
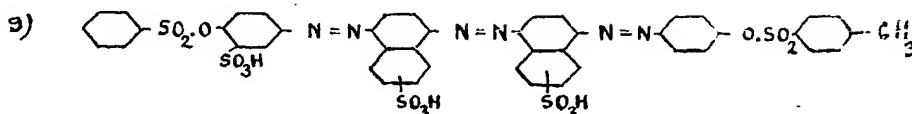
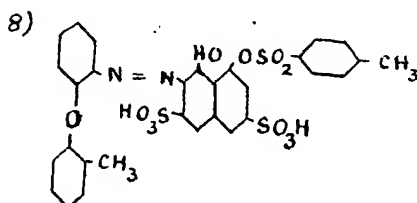
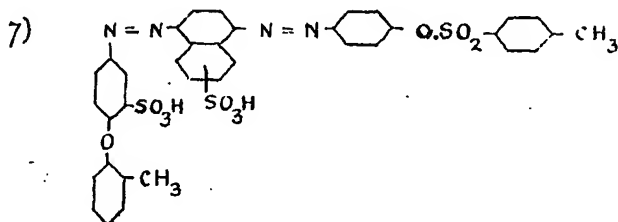
In the following table there are enumerated some compounds which are produced by a process according to the invention and similar to that set out in any of the above examples:

| Acid Dyestuff No. | Basic Dyestuff | Colour Shade | |
|-------------------|---|--|-----|
| 1 | rhodamine 6G | yellow-orange | 85 |
| 2 | rhodamine B | blue-violet | |
| 3 | rhodamine B | red-violet | 90 |
| 4 | rhodamine B rhodamine 6G | bluish red eosinlike | |
| 5 | rhodamine 6G rhodamine B setoflavin T (Schultz Vol. 2, p.197) auramine OO | yellow-red red yellow-orange yellow | 95 |
| 6 | rhodamine B rhodamine 6G | bluish red yellowish red | 100 |
| 7 | setoflavin T | yellow-orange | |

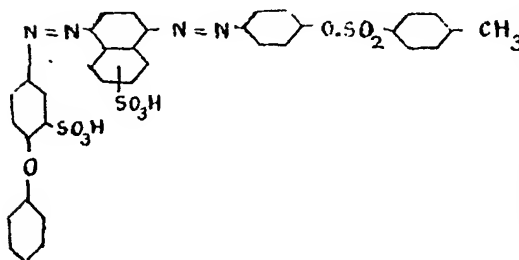
| | Acid Dyestuff | | | Basic Dyestuff | | | |
|---|---------------|--|---------------------------------|----------------|-----------------------------|----------------------|----|
| | No. | Basic Dyestuff | Colour Shade | No. | Basic Dyestuff | Colour Shade | |
| | 8 | rhodamine B | blue red | 10 | rhodamine B rhodamine 6G | red yellowish red | 10 |
| 5 | 9 | rhodamine B rhodamine 6G auramine 00 | bluish red red red orange | | auramine 00 | red yellow-brown | 15 |

COMPILATION OF THE ACID DYESTUFFS Nos. 1—10.





EXAMPLE 4.
40 parts of the dyestuff



are combined as 4% solution at 50° with
a 4% solution of 10 parts of rhodamine
6 G extra. It is allowed to cool to 30°
and is treated gradually with a 10%
solution which contains 6 parts of *p*-
toluidine, 6 parts of *N*-phenyl biguanide
(C₆H₅.NH—C(NH)—NH=C(NH)—NH₂)
and 12 parts by volume of 80% acetic
acid. At the end the temperature is
again increased, to 45°, whereupon the
precipitate changes into fine powder
form. Finally filtering is carried out and
brief washing. 43 Parts of a brown
powder is obtained of which 10% is

soluble in alcohol and nitro-cellulose
lacquers. The colour shade of the lacquer
colorations is somewhat yellower than in
the case of the corresponding dyestuff,
which is produced from the acid and
basic dyestuff only, the light fastness
however is equally good.

EXAMPLE 5.

7.3 Parts of auramine O and 1 part of
rhodamine 6 G extra are dissolved in 250
parts of water and the solution is added
slowly at 50°, whilst thoroughly stirring,
to a 4% solution of 40 parts of the acid
dyestuff according to Example 1. The
temperature is then allowed to fall to
30° and treatment is effected gradually
with 100 parts by volume of a solution
prepared from 5 parts of *p*-toluidine, 5
parts of *N*-phenyl biguanide (as in (4))
and 10 parts by volume of 80% acetic
acid. It is advisable at the end to raise
the temperature to 45°, whereby the form
of separation is influenced favourably.
After filtering off and drying 40 parts of
an orange-brown powder are obtained
which possesses the same properties as the
spirit-soluble dyestuff according to
Example 1.

Instead of the acid and basic dyestuffs

used in Examples 4 and 5, the compounds mentioned in Examples 1 to 3 and in the table may be used equally well.

Instead of *p*-toluidine and *N*-phenyl biguanide other known bases, such as for example sym.-di-phenyl guanidine, sym.-di-*o*-tolylguanidine, cyclohexyl phenyl amine, dicyclohexyl amine and so forth, which are known for the precipitation of acid dyestuffs, may be used equally well.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. The manufacture of alcohol-soluble dyestuffs insoluble in water consisting in precipitating an azo dyestuff, containing at least one acid group rendering it water-soluble, and also containing at least one hydroxyl group acylated by an aryl sulphonic acid, with or by means of a basic dyestuff.

2. Manufacture as claimed in claim 1, wherein the azo dyestuff contains more than one water-soluble rendering acid group.

3. A modification of the manufacture claimed in claim 1, where an azo dyestuff

containing more than one sulphonic acid group is used, consequently requiring more than a molecular quantity of basic dyestuff for precipitation, consisting in reducing the quantity of basic dyestuff to about an equimolecular amount, and using one or more other organic bases to make up the basic balance necessary for effecting the precipitation.

4. Manufacture of alcohol-soluble dyestuffs insoluble in water by a process substantially as hereinbefore described with reference to any of the Examples or to the Table.

5. An alcohol-soluble dyestuff insoluble in water whenever prepared or produced by the process of manufacture hereinbefore particularly described and ascertained, or by any process forming the obvious chemical equivalent thereof.

6. Colorations whenever produced by the application of an alcohol-soluble dyestuff insoluble in water as claimed in claim 5.

Dated the 20th day of January, 1942.

For the Applicants,
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Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1943.

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